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THE CONROTATORY RING OPENING OF *cis*-BICYCLO[4.2.0] OCT-7-ENE. I. TRAPPING *cis*, *trans*-1,3-CYCLOOCTADIENE WITH DIMETHYL ACETYLENEDICARBOXYLATE.

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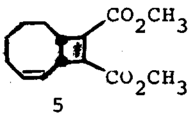
The ring opening of *cis*-bicyclo[4.2.0] oct-7-ene, **1**, to *cis*, *cis*-1,3-cyclooctadiene, **2** has been thoroughly studied in the last few years.[1,2] The reaction proceeds at a reasonable rate only at temperatures near 250°. The high activation energy of the reaction is consistent with the theory of Woodward and Hoffmann[3] which predicts that disrotatory ring opening of a cyclobutene should be an unfavorable process. The corresponding Woodward-Hoffmann allowed process, conrotatory ring opening to *cis*, *trans*-1,3-cyclooctadiene, **3**, has not been observed although the reverse reaction occurs readily at 80°.[4-6] Thus, it seemed likely to us that conrotatory ring opening ($\mathbf{1} \rightarrow \mathbf{3}$) does occur at temperatures much lower than those necessary for the disrotatory opening, but that the reaction had not been observed because the equilibrium between the cyclobutene and the diene lies far to the left. We wish to present evidence supporting this viewpoint.

2 **1** **3**

When **1** and dimethyl acetylenedicarboxylate, **4**, were mixed at 50° no reaction ensued. However, heating a mixture of **1** and **4** to 110° gave a complex mixture of esters. The same mixture of esters was produced when **3** and **4** were allowed to react at 50° and then the reaction mixture was heated to 110°. These three experiments offer evidence that **1** does undergo conrotatory ring opening to **3**.

In order to ascertain the nature of the addition products, the following experiments were conducted. (I) The *cis*, *trans*-diene, **3**, was allowed to react with dimethyl acetylenedicarboxylate, **4**, in refluxing pentane and then the crude reaction mixture, consisting of *cis*-and *trans*-dimethyl bicyclo-[6.2.0]deca-2,9-diene-9,10-dicarboxylates, **5** and **6**,[7] was hydrogenated[8] to give a mixture which was 48% *trans*, *cis*-dimethyl bicyclo-[6.2.0]-decane-9,10-dicarboxylate and 52% of the combined *cis*, *anti*, *cis* and *cis*, *syn*, *cis* isomers.[9-10]



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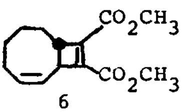

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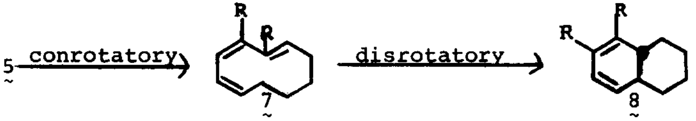
(II) When 5 and 6 were heated in refluxing toluene for 13 hours they partially rearranged. The components of the new mixture were identified as 5, 6, dimethyl-*trans*, *cis*, *cis*-cyclodeca-1,3,5-triene-2,3-dicarboxylate, 7, and dimethyl *trans*-bicyclo[4.4.0]deca-2,4-diene-2,3-dicarboxylate, 8. Compounds 7 and 8 arise from 5 as shown below.[12] Compound 6 (the *trans*-isomer) appears to be stable under these conditions. Very little isomerization of 6 was noted even after 45 hours in refluxing xylene.[13]



R = CO_2CH_3

(III) The distilled adduct mixture containing 5, 6, 7 and 8, was unstable, undergoing ready resinification. A combination of gas chromatography and mass spectrometry showed that all of the adducts had parent ions at M/e = 250 and had fragmentation patterns consistent with the assignments of structures 5, 6, 7 and 8. The crude distillate was hydrogenated,[7,8] hydrolyzed by base, acidified and then decarboxylated electrolytically to produce a mixture of olefins.[14,15] The olefin mixture was hydrogenated to produce a mixture of hydrocarbons which were direct descendants of the diesters 5, 6, 7 and 8 and serve to identify them.[16]

(IV) When a toluene solution of 7 (0.5M) and 4, (1.0M) was heated at reflux for 64 hours, 53% of the starting olefin was consumed. Analysis of the product mixture showed the presence of a 33% yield[17] of a mixture of isomers identical to that obtained from 3 and 4 along with a 21% yield[17,18] of *cis*-1,3-cyclooctadiene. A considerable quantity of unidentified high boiling material was also produced. Similar results were obtained in refluxing xylene (16 hours) but virtually no reaction was observed after several days refluxing in benzene.[19]

The accompanying paper presents kinetic data and offers an hypothesis to account for the apparent disrotatory opening of 1 and related [n.2.0] systems.[20]

REFERENCES AND FOOTNOTES

1. R. Criegee, D. Seebach, R. E. Winter, B. Borretzen, and H. A. Brune, *Chem. Ber.*, 98, 2339 (1965).
2. G. R. Branton, H. M. Frey, and R. F. Skinner, *Trans. Faraday Soc.*, 62, 1546 (1966).
3. R. Hoffmann and R. B. Woodward, *Accounts of Chem. Res.* 1, 17 (1968).
4. K. M. Shumate, P. N. Neuman, and G. J. Fonken, *J. Am. Chem. Soc.*, 87, 3996 (1965).
5. R. S. Liu, *ibid.*, 89, 112 (1967).
6. Conrotatory opening of a *trans*-bicyclo[4.2.0] oct-7-ene has been reported; J. J. Bloomfield, *Tetrahedron Letters*, 587 (1968).
7. Essentially identical results have been reported recently by P. G. Gassman, H. P. Benecke and T. J. Murphy, *Tetrahedron Letters*, 1649 (1969).

8. Over 5% Pd/C at 100° and 1000 lbs. hydrogen pressure.
9. The authentic compounds were prepared by photoaddition of maleic anhydride to cyclooctene, with the sterochemistry being established by equilibration experiments and nmr spectra, following the procedure used in a similar study on the cyclohexene-maleic anhydride photoadducts.[9]
10. R. Robson, P. W. Grubb, and J. A. Barltrop, *J. Chem. Soc.*, 2153 (1964).
11. A benzene solution of tetracyanoethylene and **3** underwent an exothermic reaction to give a dark red solution and a white crystalline adduct, m.p. 169.5-171.5°. The adduct was identified by nmr, IR, and elemental analysis as 9,9,10,10-tetracyano-*cis*-bicyclo[6.2.0]-dec-6-ene.
12. *cf.*, P. Radlick and W. Fenical, *Tetrahedron Letters*, 4901 (1967).
13. The thermal stability of **6** is probably related to the higher degree of strain in the all *cis*-cyclodecatriene (as revealed by model studies) than in **6**.
14. E. J. Corey and J. Casanova, Jr., *J. Am. Chem. Soc.*, **85**, 165 (1963).
15. Special applicability of this technique to the present problem has been recently demonstrated. a) P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen and T. Whitesides, *Tetrahedron Letters*, 5117 (1968) and b) H. H. Westberg and H. J. Dauben, Jr., *ibid.*, 5123 (1968)., c) Gassman et al.[7] also used this method.
16. The hydrocarbons produced, a *cis*-bicyclo[6.2.0]-decane from **5** (2%), *trans*-bicyclo[6.2.0]-decane from **6** (53%), cyclodecane from **7** (36%) and *trans*-decalin from **8** (9%), were identified by comparison with known samples by peak matching and peak enhancement and by mass spectrometry. A 1/16 inch, 10 foot-long column packed with 3% SE-30 on Aeropak (Varian-Aerograph) was used at 50 to 70°.
17. Based on consumed olefin.
18. Compound **2** was also produced when **3** and **4** were heated together at 140° for only five minutes. Under these conditions some **3** is converted to **1** but **1** is not isomerized to **2** and neither **1** nor **2** react with **4**. The formation of **2** and the isomers **5** and **6** is explained by assuming that the initial adduct of **3** and **4** is a diradical (or a zwitterion) which can cyclize to **7** or **6** or fall apart to give **2**.
19. The mixture of esters in each case was degraded to mixture of hydrocarbons which had essentially the same distributions described in footnote **15**.
20. J. J. Bloomfield, J. S. McConaghy, Jr. and A. G. Hortmann, *Tetrahedron Letters*, 3723 (1969).